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Development of an automated method for modelling of bio-crudes originating from biofuel production processes based on thermochemical conversion

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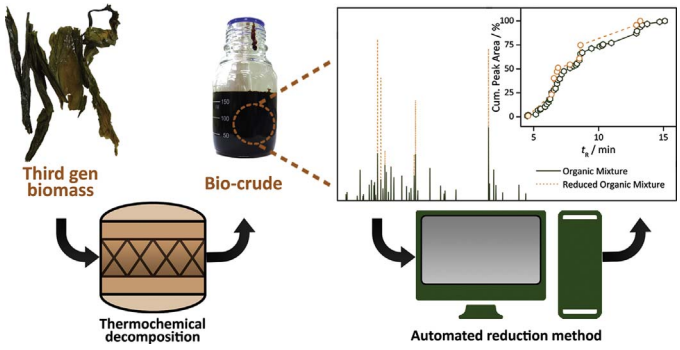
HIGHLIGHTS

- A method utilizing experimental data and producing a reduced mixture was developed.
- Software solution was developed for method automation.
- Results were tested in Aspen and validated against seven experimental datasets.
- Swift and accurate reduced representation of complex mixtures was produced.

GRAPHICAL ABSTRACT



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ABSTRACT

The prominence of biofuel research is growing as the global energy policies focus on renewable energy technologies. Accurate process design and simulation is required when evaluating technological and market capabilities of large scale, novel, fuel production processes. Thermochemical decomposition, employed in various biofuel production routes (pyrolysis, liquefaction, and so on) yields complex liquid mixtures (bio-crudes) containing numerous compounds. The process simulation of such processes must accurately represent the physical, thermodynamic and chemical properties of bio-crudes, while reducing complexity to a point where it can be handled by a process simulator in a time effective manner. In this work, a software employing automated modelling of bio-crudes based on raw experimental data, has been developed. The program output is a ready-to-use reduced mixture, including all product phases and in mass balance with the Proximate and Ultimate analyses of the feedstock biomass material. As there are many approaches to bio-crude modelling, the novelty of this method lies in the combination of the minimization of the number of components needed and the minimization of the level of artificiality introduced in the system. The automation of the method allowed for fast reduction and optimization of seven experimental data sets which were then validated by process simulation.

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1. Introduction

While fossil fuels still, without precedent, remain the life stream of modern societies, their future depletion is becoming increasingly imminent. Coupled with the large greenhouse gas surplus their consumption is producing, it is evident that a new energy carrier will soon have to replace fossil fuels. In the last two decades, biofuel research has intensified as they are being increasingly considered as a viable replacement for crude oil derivatives. In comparison to crude oil reserves, biological feedstocks for bio-fuel production are globally widespread. On the other hand, presently, biofuel production brings several disadvantages, which gave rise to scepticism towards using biofuels as suitable fossil energy replacement. Advocates against biofuels rightfully argue that large government incentives for development of feedstock (crops) and production sites gave rise to the so-called biofuel boom, which peaked in 2005 [1] and subsequently led to a rise in global food prices. These concerns gave rise for utilization of aquatic biomass for biofuel production (i.e., microalgae and macroalgae) [2–7]. Other than the obvious advantage that aquatic biomass does not require land for cultivation and that the available cultivation area is far larger, marine biomass can absorb carbon dioxide more effectively (6–8% photosynthetic efficiency) than any terrestrial biomass (1.8–2.2% photosynthetic efficiency) [8]. However, when considering large-scale fuel production, compositional disadvantages, particularly high moisture and mineral content, should be considered [9]. There are three general routes for the conversion of biomass: biological, chemical, and thermochemical. Each has its own set of advantages and disadvantages, which vary in respect to several factors such as the type of biomass, available resources, location [10].

Thermochemical processes offer the most direct conversion. Furthermore, the product phase distribution, and composition are open to modifications by varying process parameters such as temperature, pressure and heating rate [10–12]. Finally, thermochemical (as opposed to biochemical) processes can be performed in a continuous mode, which is an important advantage in terms of economics and energy savings compared to batch processes.

The accurate process simulation with regards to the thermochemical decomposition of biomass, such as pyrolysis, is challenging due to the complex nature of the products generated. The process yields products in all three phases (gaseous, liquid and solid) [13,14]. The goal of pyrolysis is to maximize the yield of the liquid phase since the desired final products are liquid fuels. Pyrolysis liquid products or bio-crudes are complex organic mixtures containing up to hundreds of compounds [15–18]. The compounds are mostly oxygenated hydrocarbons, organic acids, and other organics [15] with varying molecular masses and boiling points. Furthermore, bio-crudes, especially produced from aquatic biomass contain a comparatively large water content. Organic compounds are either, completely, semi- or non-water solvated, forming a two-phase liquid (organic and aquatic) with gradual phase transition [19]. Process simulator, such as Aspen Plus (Aspen Tech, Cambridge, MA, USA), which was used in this work, is equipped with databases containing numerous compounds with well-defined properties, needed for accurate simulation of unit operations [20]. More often than not, a large number of experimentally identified compounds cannot be found in the databases or if they can be found, their properties may not be well defined. Furthermore, one of the common issues in the simulation of bio-crudes is defining a mixture with a minimum number of compounds, which, in all respects (chemical composition, density, heating value, and so on.), accurately represent the complex bio-crude mixtures [21–23]. Finally, the reduced mixture representing the liquid product, together with products from other phases, must be in atomic mass balance with the feedstock.

One approach to these challenges is modelling the pyrolysis kinetics using key biopolymer components [23,24]. Although this approach possesses predictive capabilities, it lacks in-built minimizing strategy of components and does not fully employ experimental data of the product characterization. Different approach to bio-crude modelling is employed by Jones et al. [21], and Bonalumi [25] where a set of pseudo-components is defined from the available components in the process simulator's database, manually mixing-and-matching to tune the properties of the reduced mixture to the original bio-crude. This may save the user time in constructing the reduced mixture, but results in a considerable reduction of accuracy. A similar approach was employed by Cruz et al. [26] where real components (components experimentally found in biocrude) and pseudocomponents were combined, with the ultimate goal of reproducing the true boiling point (TBP) curve of the bio-crude. Pseudocomponents in this research were a set of components not experimentally found in the biocrude, but instead inputted in the simulated mixture by the user to manually tune the properties of the simulated mixture or generated by a process simulator. Although some real components were used, the total number of components in the reduced mixture was large totalling 47 components, of which 40 were pseudocomponents. Another approach utilizing modelling of biocrudes via distillation curves was demonstrated by Ramirez et al. [27]. This approach utilized conventional petroleum industry techniques of generating distillation curves from GC-FID experimental data. This approach directly utilized GC-FID data for modelling of pure biocrudes and biocrude/petroleum crude blends. However, this simulation method completely utilizes process simulator generated pseudo-components, which are arguably well suited for column simulation, but differ extensively from more simplistic methodology presented in this work. Finally, Carrasco et al. [28] manually picked real components, which are known to be present in both the bio-crude and the process simulator database. This method possibly yields results the closest to the true bio-crude mixture since only real components were used. However, it does not utilize raw characterization data, and requires a great deal of tedious manual reduction. It also requires extensive a priori knowledge about bio-crude composition making its applicability and accuracy questionable.

All the above-mentioned approaches introduce a degree of artificiality and bias to the process simulation. In this work, we aimed to develop a widely applicable, user-friendly and fully automated reduction method, which directly utilizes raw experimental data. Components, which comprise the reduced mixture for bio-crude simulation, are derived from GC–MS data. They are thereby unbiased, and accurately represent the original mixture over key characterization parameters while their number is minimized. As the time required for the manual execution of this method and similar methods is considerable (up to two hours per dataset on average), a software has been developed to automate the procedure. The outputs of the software, in a spreadsheet form, are not only the reduced mixture representing liquid, the pyrolysis product, but also a ready-to-use process simulator input, in which the atomic composition of the biomaterial (feed) is in optimal mass balance with the complete set of products of thermochemical decomposition. This alleviates the need for the time consuming, manual reactor balancing.

2. Materials and methods

2.1. Experimental techniques

2.1.1. Pyrolysis process

The method was tested on seven datasets, originating from published works by Choi et al. [29–31]. In them, brown macroalgae *Saccharina japonica* was subjected to pyrolysis for investigation in biofuel application. Pyrolysis was performed in fixed- and fluidized-bed reactors under various process conditions (temperature, heating rate, fluidizing velocity, and so on.). The effect of different pre-treatment routes, such as water washing, and acid washing was also reported. The optimal conditions for each reactor type and pre-treatment were determined (maximum liquid yield). The proximate and ultimate analysis of the algae was performed thus providing information on the elemental